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NOVEL EXPLOITATION OF DUBININ-ASTAKHOV THEORY IN SORPTION REACTOR DESIGN FOR REFRIGERATION AND HEAT PUMPS APPLICATIONS

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ABSTRACT

This paper describes novel methodology that is based on a single given adsorbent-refrigerant pair characteristic (example activated carbon 208C–Ammonia pair) leading to the characterization of the same adsorbent (activated carbon 208C) with various refrigerants such as Methanol, Ethanol, R723 (azeotropic mixture of 60% Ammonia and 40% Dimethyl Ether) and R744 (Carbon Dioxide). Overall, with exception of R744 (Carbon Dioxide), the results obtained shows a marginal difference compared to standard method that heavily depends on experimental data. For example with methanol, the standard method produces a maximum uptake (x_o) of 0.3676 kg methanol/kg carbon while the new method predicts 0.3740 kg methanol/kg carbon; with CO_2 both standard and new methods predict 0.3242 kg CO_2/kg carbon and 0.3850 kg CO_2/kg carbon.

1. INTRODUCTION

The design of adsorption reactors for refrigeration and heat pumps applications generally requires the mapping of refrigerant specific uptake against operating conditions mainly temperatures and pressures. A large number of experimental data for the pair studied (adsorbent-refrigerant) are often needed in order to identified the three key parameters of a modified expression of Dubinin-Astakhov equation: x_o (maximum uptake of refrigerant by the adsorbent – kg refrigerant per kg of adsorbent), k (energetic affinity characteristic of adsorbent-refrigerant pair and n (characteristic of adsorbent micro-pores size distributions) **[1-3].** Furthermore this lengthy mapping process that is useful to estimate the potential COP (coefficient of performance) is specific to a given adsorbent-refrigerant. This means for instance that with the same adsorbent, each refrigerant will require its experimental test for mapping. This paper proposes novel methodology that is based on a single given adsorbent-refrigerant pair mapping (activated carbon 208C – Ammonia pair) leading to the mapping of the same adsorbent (activated carbon 208C) with various refrigerants such as Methanol, Ethanol, R723 (azeotropic mixture of 60% Ammonia and 40% Dimethyl Ether) and R744 (Carbon Dioxide).

2. METHODOLOGY DESCRIPTION

The method proposed is articulated around a reference adsorbent-refrigerant pair as activated carbon 208C-ammonia that was initially fully tested in order to provide the adsorption characteristics. For this specific reference pair, experimental porosity tests were carried out under refrigeration and heat pumps operating conditions ($T_{Condensing}$ = 35°C and $E_{vaporating}$ = -5°C for ice making ; $T_{Condensing}$ = 35°C and $E_{vaporating}$ = 10°C for air conditioning and $T_{Condensing}$ = 40°C and $E_{vaporating}$ = 5°C for heat pumping – for all applications the bed temperature ranges from 35°C to 200°C) and the data fitted to a modified form of the Dubinin-Radushkevich (D-R) equation [2]:

$$x = x_o exp\left[-k\left(\frac{T}{T_{sat}} - 1 \right)^n \right] \quad (1)$$

where: x is the ammonia concentration (kg ammonia/kg carbon); T is the carbon temperature (K); x_o is the ammonia concentration under saturation conditions (kg ammonia/kg carbon); T_{sat} is the saturation temperature corresponding to the gas pressure (K); k is defined as the energetic affinity characteristic of adsorbent-refrigerant pair and n is the characteristic of adsorbent micro-pores size distributions **[3].**
x_o k and n are also commonly called Dubinin coefficients and for activated carbon 208C-ammonia: x_o = 03077 kg ammonia/kg carbon; $k=4.439$ and $n=1.187$ **[4].**
From now on, the adsorption characterization of activated carbon with a refrigerant different from Ammonia consists of three steps:

1) ***Evaluation of n:*** The n value provided by the unique test carried out is an intrinsic characteristic of the adsorbent: it is considered constant therefore for the activated carbon 208C, n=1.187.

2) ***Evaluation of xo:*** The adsorbed refrigerant is always assumed to be in a liquid form located in the adsorbent micro-pores **[5].** Therefore the maximum uptake of refrigerant by the adsorbent (xo) is calculated from the specific volume of micro-pores which is often provided by the adsorbent manufacturer (for activated carbon 208C, v_s = 0.500 cm^3/g) and the refrigerant liquid density at normal pressure condition or atmospheric pressure (ρ_L):

$$x_o = \rho_L v_s \tag{2}$$

3) ***Evaluation of k:*** The energetic affinity characteristic of adsorbent-refrigerant pair (k) is calculated from both gas affinity coefficient (β) and average adsorption potential energy of the adsorbent E_o (for activated carbon 208C, E_o ~ 22 kJ/mole). In fact, with Dubinin adsorption theory prospective **[1, 2],** it is established that in the Dubinin-Radushkevich (D-R) modified equation (1) the term k could be defined as **[6]**:

$$k = \left(\frac{AR_u}{\beta E_0} \right)^n \tag{3}$$

where: A is the slope of saturated adsorbate line on Clapeyron diagram; R_u is the universal gas constant (R_u = 8.3144 J/mole); Eo is adsorption potential energy of adsorbent (J/mole); gas affinity coefficient and n is the characteristic of adsorbent micro-pores size distributions.

3. RESULTS AND DISCUSSIONS

The key characteristics of the four refrigerants (Methanol, Ethanol, R723 (azeotropic mixture of 60% Ammonia and 40% Dimethyl Ether) and R744 (Carbon Dioxide or CO_2)) used to test the proposed method are presented in **Table 1**. The estimated values of Dubinin coefficients are given in **Table 2**. By comparing the current coefficients (mainly activated carbon 208C with both Methanol and CO_2) with those obtain from standard method through coefficient identification with experimental data, we could observe that overall the differences between coefficients are marginal as show in **Table 3** with the exception of the maximum uptake with R744 (CO2) which presents a difference of 0.0608 kg /kg (corresponding to relative value of about 19%). In fact, due to the nature of R744 (CO2), it has a pressure window in liquid form ranging about 5 bar to 74 bar therefore impossible to consider its liquid density at atmospheric pressure. For this specific reason, x_o for CO2 is calculated with liquid density taken at ambient temperature of 20°C (about 57 bar).

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	Methanol	**Ethanol**	**R723**	**R744 (CO2)**
β	0.40	0.61	0.335	0.35
ρ_L **(kg/m^3)**	748	757	708	770 (*)
A	4631.1	5040.3	2689.6	1988.3

Table 1: Refrigerants properties (* Density taken at ambient temperature of 20°C)

Refrigerants	**Methanol**	**Ethanol**	**R723**	**R744 (CO2)**
x_o **(kg/kg)**	0.3740	0.3785	0.3540	0.3850
k	5.7665	3.8638	3.7342	2.4768
n	1.187	1.187	1.187	1.187

Table 2: Dubinin coefficients from the proposed method

Refrigerants	Methanol			R744 (CO2)		
Method	Standard	New	*Difference*	Standard **[7]**	New	*Difference*
x_o (kg/kg)	0.3676	0.3740	*0.0064*	0.3242	0.3850	*0.0608*
k	6.3147	5.7665	*-0.5282*	2.5135	2.4768	*-0.0370*
n	1.180	1.187	*0.007*	1.1602	1.187	*-0.0268*
SEE (kg/kg)	0.0045	N/A	*N/A*	0.0087	N/A	*N/A*

Table 3: Methods comparison

4. RESULTS EXPLOITATION

As example exploitation of the results already presented, the cooling performance of an adsorption system are estimated. This estimation is carried out with activated carbon 208C-R723 refrigerant pair under typical operating conditions: condensing temperature T_C = 35°C, evaporating temperature T_E = -5°C and initial bed temperature T_1 = 35°C for ice making and T_C = 35°C, T_E = 10°C and T_1 = 35°C for air conditioning. The driving temperature is 150°C. The cooling energy $Q_{cooling}$ (kJ/kg carbon) is estimated as:

$$Q_{cooling} = L\Delta x$$

Where: L is the refrigerant specific latent heat (kJ/kg R723) and Δx is the uptake swing during the desorption phase (kg R723/kg carbon).

The estimation of cooling energy values are 128 kJ/kg carbon and 153 kJ/kg carbon for ice making and air conditioning applications respectively (see). As expected, the cooling energy decreases with the evaporating temperature since both condensing and driving temperatures are fixed. In other words, for this specific case, the cooling energy is mainly driven the uptake swing as shown in **Figure 1**.

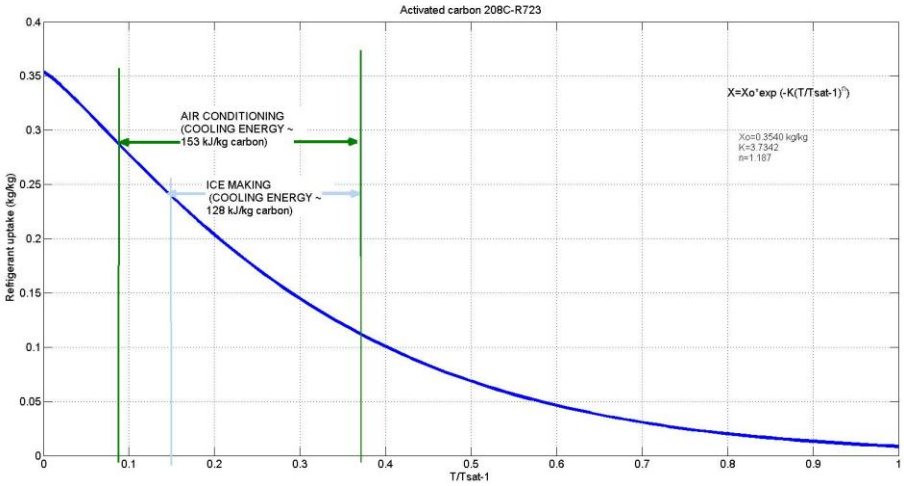

Figure 1: Refrigerant uptake profile and cooling performance.

5. CONCLUSIONS

A novel methodology that is based on a single given adsorbent-refrigerant pair characteristic (example activated carbon 208C–Ammonia pair) leading to the characterization of the same adsorbent (activated carbon 208C) has been described. The new method is tested with Methanol, Ethanol, R723 (azeotropic mixture of 60% Ammonia and 40% Dimethyl Ether) and R744 (Carbon Dioxide). Overall, with exception of R744 (Carbon Dioxide), the results obtained shows a marginal difference compared to standard method that heavily depends on experimental data. For example with methanol, the standard method produces a maximum uptake (x_o) of 0.3676 kg methanol/kg carbon while the new method predicts 0.3740 kg methanol/kg carbon; with CO_2 both standard and new methods predict 0.3242 kg CO_2/kg carbon and 0.3850 kg CO_2/kg carbon respectively. The proposed methodology offers the possibility to characterize an adsorbent using less hazardous gases such as Nitrogen (N_2) or Helium (H_e) and rapidly screen its potential with a range refrigerants or the desired initial refrigerant.

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